SULFUR CAPTURE AND NITROGEN OXIDE REDUCTION ON THE 6' X 6' ATMOSPHERIC FLUIDIZED BED COMBUSTION TEST FACILITY

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INTRODUCTION

Atmospheric fluidized bed combustion (AFBC) is being developed as a cost-effective, low-polluting method of direct coal utilization for electric power generation. An earlier state-of-the-art assessment (EPRI Final Report FP-308) concluded that the existing AFBC data base was inadequate for the design of utility-scale units -- that is, the available data were limited in scope, and since they had been derived mainly from laboratory-scale equipment, it was doubtful whether they could be applied to the design of utility boilers. The need for a large, well- instrumented facility capable of long-term testing was clearly indicated.

As a result, a 6-foot x 6-foot (6' x 6') AFBC Development Facility was built at The Babcock & Wilcox Research Center in Alliance, Ohio. A complete description of the facility design details are contained in EPRI Final Report CS-1688.

PROJECT RESULTS

Construction of the 6' x 6' facility was completed in October 1977. Following a 5-month startup and debugging phase, the first test series was begun in April 1978. Since then, approximately 2000 hours of testing per year have been logged at the facility. The facility has demonstrated the capability for long-term, steady-state operation, with tests typically lasting from 300 to 500 hours. The AFBC unit is large enough to result in gas-solid residence times for the various zones of the combustor that are typical of those expected for utility-scale units. A wide range of conditions can be tested at the facility. Also, the computerized data acquisition system has been shown to provide accurate, comprehensive documentation of the test results.

SUMMARY OF TESTS

Testing completed as of July 1981, along with a short description of each test series is summarized below:

Test Series	Date	Hours Firing Coal	Comments
1	May 1978	277	Initial characterization
2	June 1978	248	Long duration test to characterize performance
3	August 1978	278	Recycle
4	September 1978	241	Coal size variation, temperature variation
5	November 1978	204	Limestone and coal size variation, temperature variation
6	February 1979	406	New distributor plate, Battelle emission testing - Pittsburgh #8 coal
7	March 1979	171	Single coal feed point - 36 ft^2, bed depth variation, coal and limestone variation
8	May 1979	427	Recycle; underbed single point, temperature variation
9	June 1979	298	Coal size variation, temperature variation
10	July 1979	194	Recycle; overbed and 4-point underbed with coal and limestone
11	August 1979	96	Pulverized coal
12	December 1979	265	New in-bed tube bundle, new baghouse, GCA emission testing - Pittsburgh #8 coal
13	January 1980	318	Recycle; underbed single point, limestone size variation, excess transport air
14	February 1980	277	Recycle; underbed single point and overbed, slumped bed heat transfer study test
15	April 1980	382	Fuller Kinyon pump characterization, baghouse recycle, lignite test
16	May 1980	147	Turndown (slumping) test
17	June 1980	344	Limestone size variation, center recycle
18	July 1980	326	New distributor plate, 4 ft/sec characterization test
19	October 1980	365	4 ft/sec testing, recycle
20	December 1980	344	Feed nozzle design testing, 8 ft/sec
21	January 1981	170	Feed nozzle design testing, 8 ft/sec
22	March 1981	380	NO_x reduction tests
23	June 1981	485	12 ft/sec testing

Significant data were generated in the areas of fly ash recycle, coal particle size, limestone particle size, 5 ft/sec, 8 ft/sec, and 12 ft/sec fluidizing velocity operation, combustion of lignite, and nitrogen oxide reduction. Testing continued to emphasize fly ash recycle as a means of improving combustion efficiency and sulfur capture. In addition to center underbed recycle, overbed recycle with gravity and pneumatic feed as well as baghouse ash recycle configurations were tested. Recycled fly ash testing continued to result in combustion efficiencies on the order of 98%. The highly successful lignite test resulted in combustion efficiencies approaching 99%. The lignite test proved the capability of a fluidized bed combustor (FBC) to combust fuels which can be troublesome. One test was devoted to testing feed nozzles designed to prevent feedline pluggage during slumping. A power outage simulation test was also carried out. The test was designed to determine minimum flow rates through the in-bed tube bundle required to prevent tube overheating during a power outage. Results indicated that tube overheating may be prevented with minimal design considerations.

Tests were also conducted to evaluate bed height reduction as a means of load control in an AFBC facility. These variable bed height tests provided the data needed to design an automatic load control system that will be installed on the 6' x 6' in 1982.

One series of tests was devoted to two-stage combustion, i.e., allowing a portion of the forced draft air to bypass the bed, recombining with the fluidizing gas in the freeboard region. These tests, aimed at NO_x reduction, are discussed later in this paper.

A significant amount of data covering AFBC have been generated on the 6' x 6'. Some of these data have been summarized and discussed in various technical papers and, therefore, will not be repeated in this paper. Sulfur capture and nitrogen oxide reduction are the two items that will be discussed in the following sections.

SULFUR CAPTURE

No Fly Ash Recycle

Numerous non-recycle tests have been run on the 6' x 6' AFBC at a fluidizing velocity near 8 ft/sec. This large data bank provides information enabling a better understanding of sulfur capture with various operating parameters. A plot of percent sulfur removal versus calcium-to-sulfur ratio showed that sulfur removal is a strong function of the amount of fresh limestone feed (Figure 1). However, the data is quite scattered, indicating that other factors such as particle size, entrainment loss, bed temperature, coal combustion, and sulfur release level may also have a significant influence on sulfur capture efficiency. To more thoroughly investigate these factors, data from a narrow range of Ca/S ratio were subjected to analysis. Sulfur removal was shown to be related to the size of limestone being fed into the unit (Figure 2). The plot indicates that larger limestone feed sizes result in a decreased ability to remove sulfur, a trend which is most pronounced at higher Ca/S values. This suggests that the effect of the fresh limestone feed is predominant since the spent bed lime utilization in these tests range between 23% and 40%. Consequently, the rate of sulfur capture for the bed material is many times smaller than for freshly calcined limestone at all size ranges that exist within the FBC unit. For average limestone feed sizes below 1200 microns (weight-mass average), a significant drop in sulfur retention occurred as a result of high elutriation loss of limestone feed. Further analyses were performed by restricting both the Ca/S ratio and limestone feed size. The data scatter, evident in Figure 2, was found to be related to the effects of bed particle size, extent of bed lime utilization, and bed voidage (Figures 3 and 4). Sulfur removal decreases with:

1. An increase in bed particle size for a narrow range of bed lime utilization (0.30 - 0.33).

2. High bed lime utilization.

3. Higher bed voidage.

Also, spent bed lime utilization is related to both residence time and Ca/S feed ratio, reaching 35% with a residence time of 13 hours at a Ca/S of 2.5 (Figure 5).

Increasing the fluidizing velocity to 12 ft/sec resulted in lower sulfur capture, as shown in Table 1. We believe the causes of this reduction to be: 1) higher elutriation of limestone from the bed, and 2) increased freeboard combustion of coal and its volatile matter. The table shows that carbon and limestone carryover losses were 12% and 55%, respectively. These are about 50% and 34% more than the loss at 8 ft/sec, respectively.

Reducing fluidizing velocity to about 5 ft/sec generally resulted in an improvement in sulfur capture. This was due to smaller limestone feed size and lower elutriation loss (Table 2). In addition, spent bed lime utilization reached 40%.

Table 1

Comparison of Sulfur Capture Efficiency and NO_x Emissions for 8 ft/sec and 12 ft/sec Fluidizing Velocities Under Similar Conditions of: 1) Non-Recycle and 2) Ca/S : 2.4 - 2.8

Item	Fluidizing Velocity 8 ft/sec	12 ft/sec
%SO_2 Capture	78.5	46.2
Combustion Efficiency - %	92	88
NO_x - ppm	285	158
CO - ppm	106	1696
Bed Voidage	0.62	0.72
Limestone Feed Size (weight mean average)	2908μ	984μ
Spent Bed Size (weight mean average)	2337μ	1279μ
Spent Bed Lime Utilization - %	31	29
Elutriation of Available Lime Per Limestone Feed	41	55
Elutriation of Carbon Per Carbon Feed From Coal	8	12

Table 2

Comparison of Sulfur Capture Efficiency and NO_x Emissions for 5 ft/sec and 8 ft/sec Fluidizing Velocities Under Similar Conditions of: 1) Non-Recycle and 2) Ca/S : 1.6 - 1.8

Item	Fluidizing Velocity 5 ft/sec	8 ft/sec
%SO_2 Capture	58	54
Combustion Efficiency - %	94	92
Spent Bed Lime Utilization - %	40	33
% Carbon in Carryover Per Carbon Feed	7.7	9.6
NO_x - lb/MKb	0.22	0.39
Bed Voidage	0.55	0.66
Limestone Feed Size (weight mean average)	815μ	1200μ
Spent Bed Size (weight mean average)	923μ	824μ
CO in Stack Gas - ppm	173	126

Fly Ash Recycle

Operation of the 6' x 6' since May 1979 has emphasized fly ash recycle operation. Recycle has generally improved sulfur capture as shown on Figure 6. Generally speaking, for a given test condition and a narrow range of limestone to coal feed rate, one expects the total available mole of calcium to each mole of coal sulfur to increase as the recycle ratio (recycle rate/coal rate) increases (Figure 7a). The total available calcium oxide is defined as the combined calcium oxide from the limestone feed and the unreacted calcium oxide in the recycle stream; it is designated as $(CaO)_R + (CaO)_L$. The available calcium oxide can change by varying the limestone feed rate or the recycle ratio.

Figure 7b is a plot of the expected trend of the effect of recycle ratio on sulfur capture for two different Ca/S feed ratios. Ideally, for a given set of conditions, sulfur capture should increase with increasing recycle ratio due to an increase in the total available calcium-to-sulfur ratio. The rate of increase in sulfur capture (slope of the curve) will gradually diminish as the reactivity of the recycled lime decreases due to higher calcium utilization. As the curve begins to level off, a point is reached beyond which any further increase in the recycle rate has little benefit on sulfur capture. The recycle ratio for which this occurs should increase as:

1. The particle size of the recycle stream decreases since the smaller lime size results in better reactivity at higher calcium utilization levels.

2. The limestone feed rate increases (higher Ca/S ratio). High limestone feed rates generally result in greater elutriation of freshly calcined limestone. This helps to increase the reactivity of the recycle stream, thus promoting SO_2 capture.

3. The reactivity of recycled lime improves. The improvement can be achieved through either grinding or partial hydration.

The recycle analysis was conducted by first choosing all tests with and without recycle. The data were compared by restricting the Ca/S feed ratios to narrow ranges. Figure 8 shows that the available calcium-to-sulfur ratio, $[(CaO)_L + (CaO)_R]/S$, increases dramatically as the recycle-to-feed ratio is increased. Figure 9 shows the effect of recycle on sulfur capture at three Ca/S ratios. Figure 10 shows that 90% sulfur capture can be obtained at a recycle-to-coal ratio of about 1.3 with a Ca/S feed ratio of 2.5 - 2.9.

By extrapolation, a recycle ratio of about 4 - 5 will be required at a Ca/S feed ratio of 1.5 - 2.0.

Figure 11 shows sulfur capture as a function of fluidizing velocity for both the non-recycle and recycle operating conditions. Note the significant decrease (approximately 20 percentage points) in sulfur capture for the high fluidizing velocity (12 ft/sec) tests as compared to the 8 ft/sec tests. The major reason for this reduction is attributed to the increased freeboard combustion. This, of course, causes more sulfur release in the freeboard.

NITROGEN OXIDE REDUCTION

Single-Stage Combustion

The mechanism of NO_x formation in an AFBC unit is extremely complicated, involving the formation and destruction of NO_x through various chemical reactions that occur in the bed and in the freeboard. Thus, it depends upon the coal devolatization rate and its volatile content, excess air, bed temperature, CO and SO_2 concentrations in the emulsion phase, and the bed hydrodynamics.

At 8 ft/sec fluidizing velocity, NO_x emissions were generally in the 300 ppm - 400 ppm range. However at 5 ft/sec, the NO_x was found to change with the Ca/S feed ratio as shown on Figure 12. It is believed that this effect is a result of the following mechanisms as noted by Exxon [1]:

$$CaO + SO_2 \longrightarrow CaSO_3$$

$$CaSO_3 + 2NO \longrightarrow CaSO_3\ (NO)_2$$

$$CaSO_3\ (NO)_2 \longrightarrow CaSO_4 + N_2 + 1/2\ O_2$$

As pointed out by Exxon's study, the above mechanisms could only occur in the presence of sulfated lime and with a deficit of oxygen. The rate of NO_x reduction was found to be directly proportional to concentrations of both NO and SO_2 in the gas phase as follows:

$$\frac{1}{W} \quad \frac{d(NO)}{dt} = K\ (NO)^n \ (SO_2)^m$$

Where W is the bed weight and n has a value between 0.53 - 0.67 for the temperature range of 1400° - 1600°F. The proposed mechanisms qualitatively appear to provide an explanation to our observation for the low velocity tests. It is generally believed that the relatively smaller spent bed size in these tests resulted in a fast bubbling bed with the relative excess gas velocity $(U - U_{mf})/U_{mf}$, ranging from 8 to 12. Consequently, a majority of oxygen along with air would bypass the emulsion phase via the bubble phase, resulting in a reducing atmosphere in the emulsion phase that enhanced the NO_x reduction through the mechanisms proposed by Exxon.

The NO_x emission data taken from non-recycle tests with Ohio #6 coal and 8 ft/sec fluidizing velocity appeared related to the operating excess air. However, the results were quite scattered, especially at levels below 25% excess air (Figure 13). These scattered NO_x data were found to be associated strongly to the extent of the reducing condition in AFBC where the NO_x level was usually below 200 ppm if the CO concentration in the stack gas exceeded 200 ppm (Figure 14). Further analysis of the data indicated that the high NO_x emissions were associated closely with the bed voidage, where the effect became more pronounced at higher oxidizing conditions (Figure 15).

The effect of carbon loading in the freeboard on NO_x reduction was quite evident at a high fluidizing velocity (12 ft/sec) and a recycle ratio of 1.0 - 1.4. A reduction of NO_x emissions from 0.43 to 0.23 lb/million Btu was observed (Figure 16) as carbon loading increased from 14% to 19%.

Two-Stage Combustion

Staged combustion has been proposed as a means of reducing NO_x from an AFBC unit. Several investigators [2, 3, and 4] have conducted tests to quantify the NO_x reduction with staging. However, these tests were run in small units and only overall effects were measured. To aid in evaluating the effect of staging on NO_x reduction and performance variables, the 6' x 6' AFBC facility was modified to allow air injection at an elevation of 96 inches above the distributor plate. This elevation was chosen based on data from previous tests [2]. Two injection ports -- on opposite walls of the unit -- were installed with valves to control flow and an orifice to measure flow.

Tests were conducted at the conditions listed in Table 3.

Table 3

Summary of Operating Conditions and Measured Performance Variables

Condition/Variable	Test					
	1a	1b	2a	2b	3a	3b
Bed Temp, °F	1564	1546	1544	1547	1512	1553
Bed Height - inches	51.8	52.5	50.0	49.8	47.7	47.8
Superficial Velocity - ft/sec	7.3	8.0	7.1	7.1	6.5	7.0
Coal Feed - lb/hr	1887	2042	2070	2064	2192	2228
Ca/S Ratio	2.7	2.7	2.1	2.5	2.7	2.5
Recycle - lb/hr	2560	2680	2800	2920	2280	2280
In-Bed Air Flow - lb/hr	19500	21500	19400	19400	18300	18900
Overbed Air Flow - lb/hr	0	0	2300	2300	4850	4670
Flue Gas						
O_2 - %	2.9	2.9	2.9	3.1	2.9	2.7
SO_2 - ppm	170	265	562	527	461	458
CO - ppm	208	185	247	203	248	248
NO_x - ppm	416	372	195	175	88	117
Sulfur Capture - %	91.6	86.1	77.1	75.1	74.9	76.1
Combustion Efficiency - %	98.1	97.4	96.8	96.7	96.0	96.1

At each test condition, gas traverses were made at six heights along the centerline of the unit. The gas concentration profiles obtained in-bed (16 inches above the distributor plate) are shown on Figure 17. Note the peak in O_2 and the drop in other gas concentrations near the 36-inch insertion depth. This is probably due to the recycle stream which is being injected with transport air at the 36-inch distance. Profiles above the bed (in the freeboard) were considerably more uniform.

An integrated average of the profile obtained at each elevation was calculated. This average was then plotted versus distance above the distributor plate for CO, SO_2, and NO_x as shown on Figures 18, 19, and 20. There are several points that are readily apparent from these figures.

- With zero overbed air, there is a significant reaction occurring in the freeboard, e.g., reduction of CO and NO_x.
- Two-stage combustion produces the expected trends in reducing NO_x while increasing SO_2 and CO in the bed.

- The addition of air at the 96-inch elevation allows further combustion to occur in the freeboard, thus increasing SO_2 and reducing CO and NO_x.

- Reducing the NO_x level in the bed reduces NO_x throughout the process.

- Gas concentrations measured at the 240-inch elevation, using the freeboard sampling system and analysers, agree remarkably well with the similar, but completely separate, furnace outlet system and analysers.

Figure 21 shows a plot of the furnace outlet NO_x and SO_2 gas concentrations at the three test conditions -- 0%, 10%, and 20% overbed air.

CONCLUDING REMARKS

Twenty-three test series have been completed on the 6' x 6' AFBC Development Facility covering over 7100 hours of operation. Data obtained thus far have clearly shown that fly ash recycle can improve combustion efficiency to the level needed for commercial operation. Recycle also improves sorbent utilization, thus reducing the limestone needed for sulfur capture. Measured NO_x emission levels from the 6' x 6' AFBC unit are well below current EPA limits. However, two-stage combustion tests have shown that NO_x can be reduced to about 0.15 lb/million Btu. Additional work needs to be completed to improve sulfur capture and combustion efficiency with two-stage combustion.

Information obtained thus far has allowed a significant improvement in our understanding of the AFBC process and should prove useful to researchers in this field. Further, design of prototype hardware and other equipment developed and tested on the 6' x 6' should prove useful for commercial design.

REFERENCES

[1] G. A. Hammons and A. Skoop, "NO_x Formation and Control in Fluidized Bed Coal Combustion Processes," presented at the ASME Winter Annual Meeting, Washington, DC; November 28 - December 2, 1971.

[2] J. Tatebayashi, Y. Okada, K. Yano, and S. Ikeda, "Simultaneous NO_x and SO_2 Emission Reduction With Fluidized Bed Combustion", 6th International Conference on Fluidized Bed Combustion, Atlanta, GA; April 1980.

[3] T. Hirama, M. Tomita, T. Adachi, and M. Horio, "An Experimental Study for Low NO_x Fluidized-Bed Combustor Development 2 - Performance of Two Stage Fluidized-Bed Combustion"; EST, Vol. 14, No. 88; pp. 960-965.

[4] T. E. Taylor, "NO_x Control Through Staged Combustion in Fluidized Bed Combustion Systems", 6th International Conference on Fluidized Bed Combustion, Atlanta, GA; April 1980.

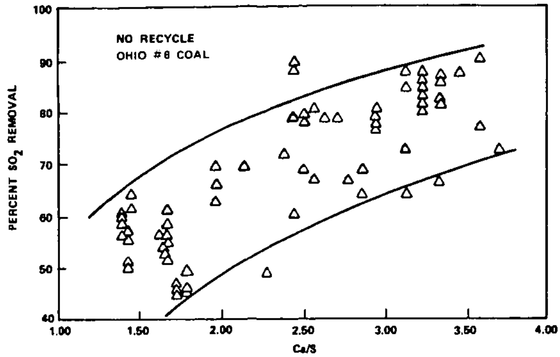


Figure 1 Sulfur Capture as a Function of Calcium/Sulfur (Ca/S) Feed Ratio

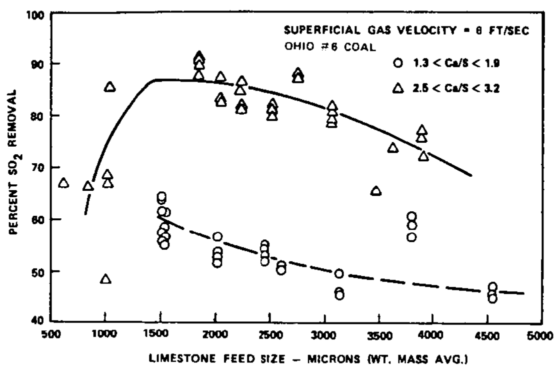


Figure 2 Sulfur Capture as a Function of Limestone Feed Size

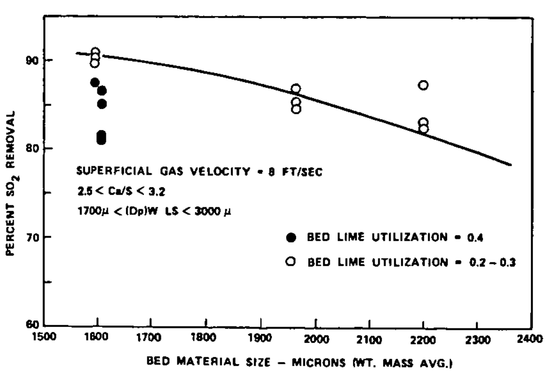


Figure 3 Sulfur Capture as a Function of Bed Particle Size

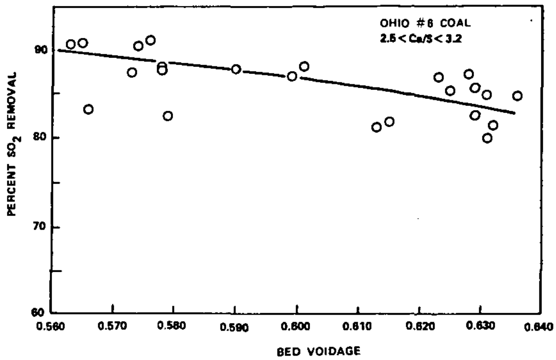


Figure 4 Sulfur Capture as a Function of Bed Voidage

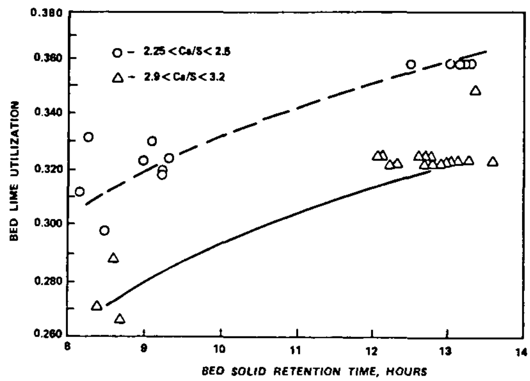


Figure 5 Bed Lime Utilization as a Function of Retention Time

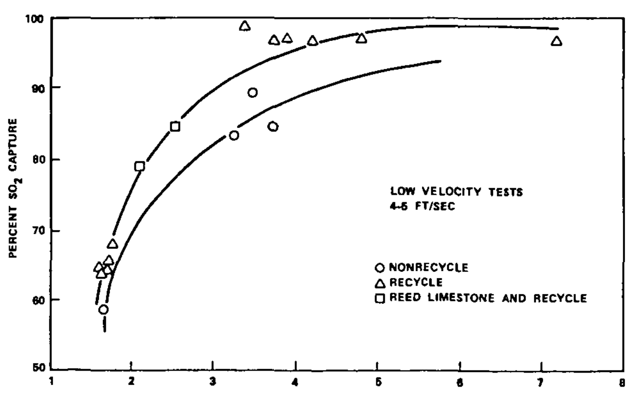
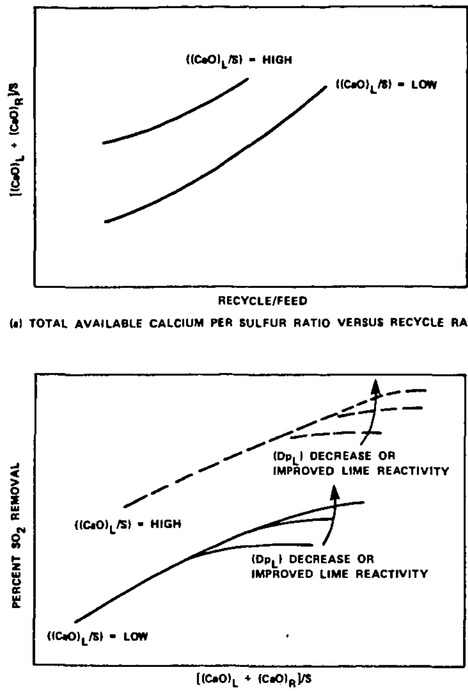


Figure 6 Sulfur Capture as a Function of Calcium to Sulfur Feed Ratio



(a) TOTAL AVAILABLE CALCIUM PER SULFUR RATIO VERSUS RECYCLE RATIO

(b) EFFECTS OF THE TOTAL AVAILABLE CALCIUM PER SULFUR RATIO ON PERCENT SO_2 CAPTURED

Figure 7 Effect of Recycle on Sulfur Capture

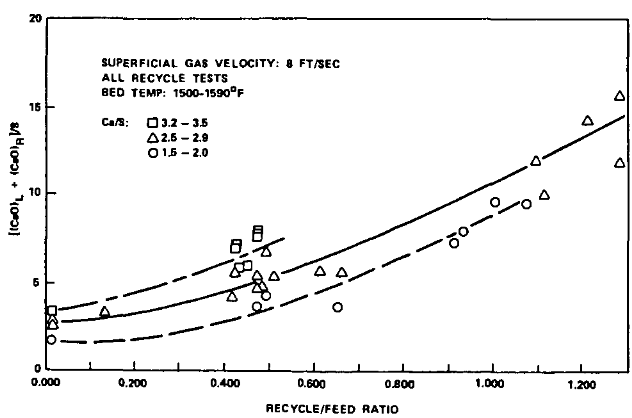


Figure 8 Effect of Recycle on the Available Calcium to Sulfur Ratio

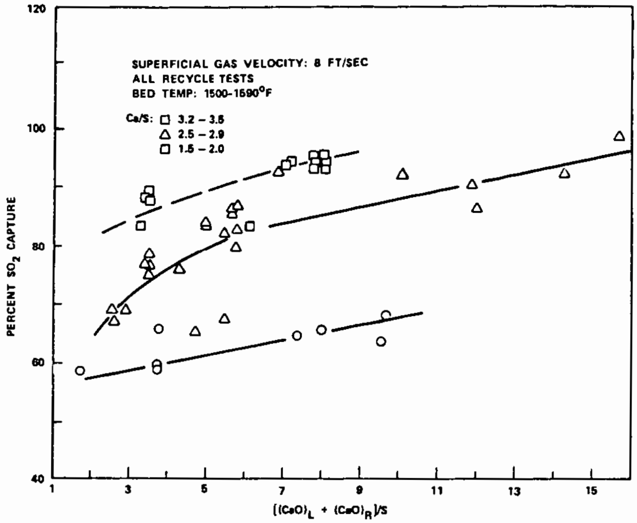


Figure 9 Effect of Available Calcium to Sulfur (Recycle) on Sulfur Capture

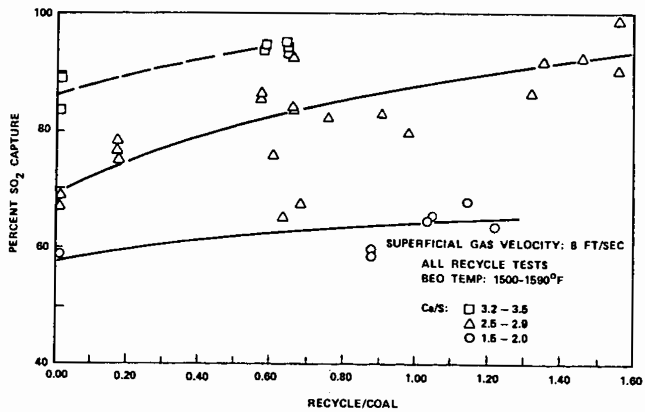


Figure 10 Sulfur Capture as a Function of Recycle Ratio

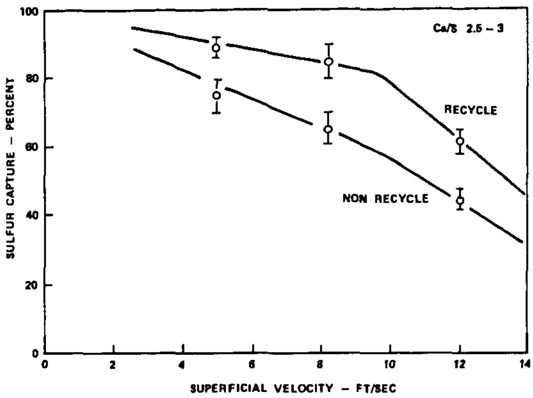


Figure 11 Sulfur Capture as a Function of Fluidizing Velocity

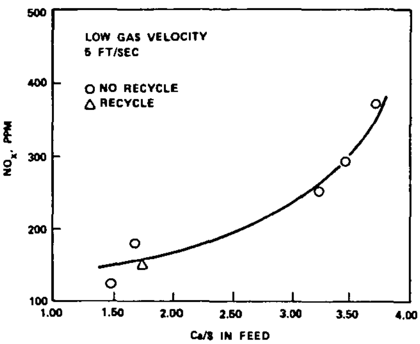


Figure 12 Nitrogen Oxide as a Function of Ca/S Feed Ratio

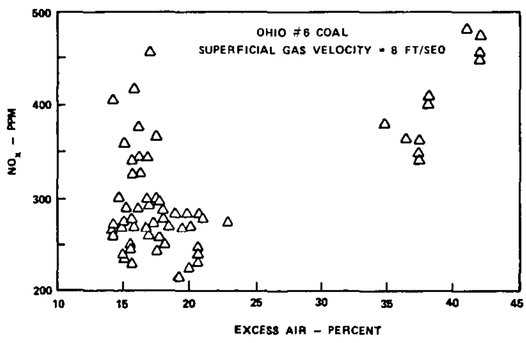


Figure 13 Nitrogen Oxide as a Function of Excess Air

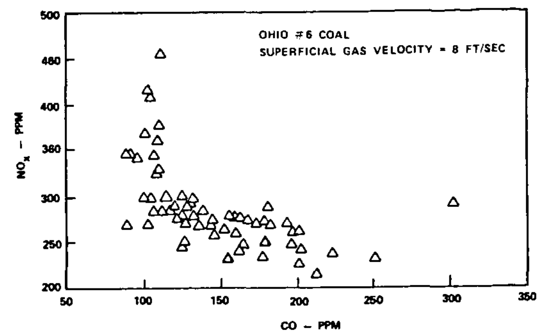


Figure 14 Nitrogen Oxide as a Function of Carbon Monoxide

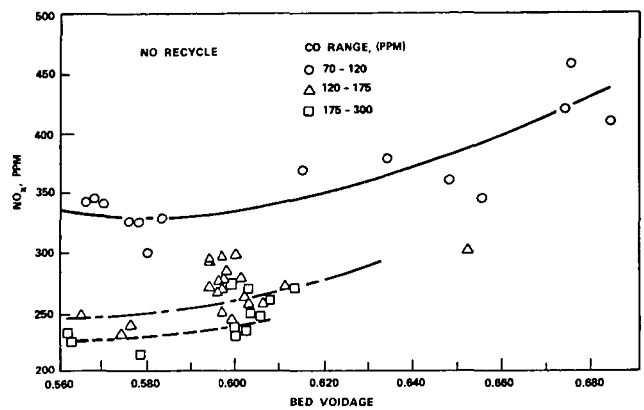


Figure 15 Nitrogen Oxide as a Function of Bed Voidage

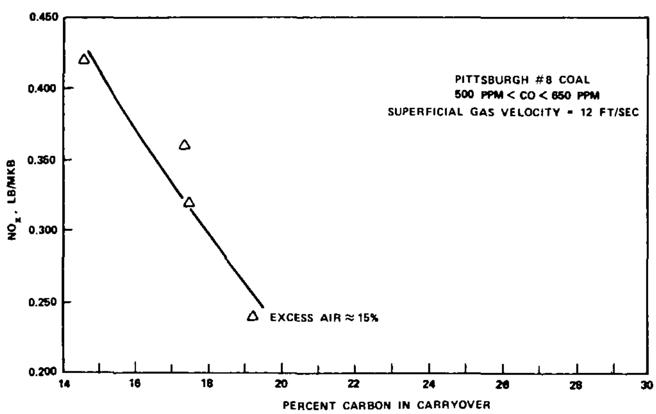


Figure 16 Nitrogen Oxide as a Function of Carbon Loading

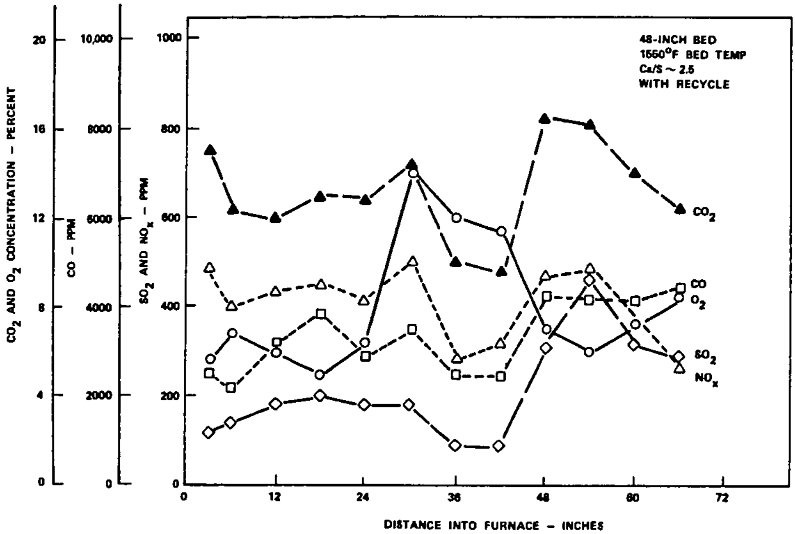


Figure 17 Gas Concentration Profiles – In-Bed (16 Inches Above the Distributor Plate)

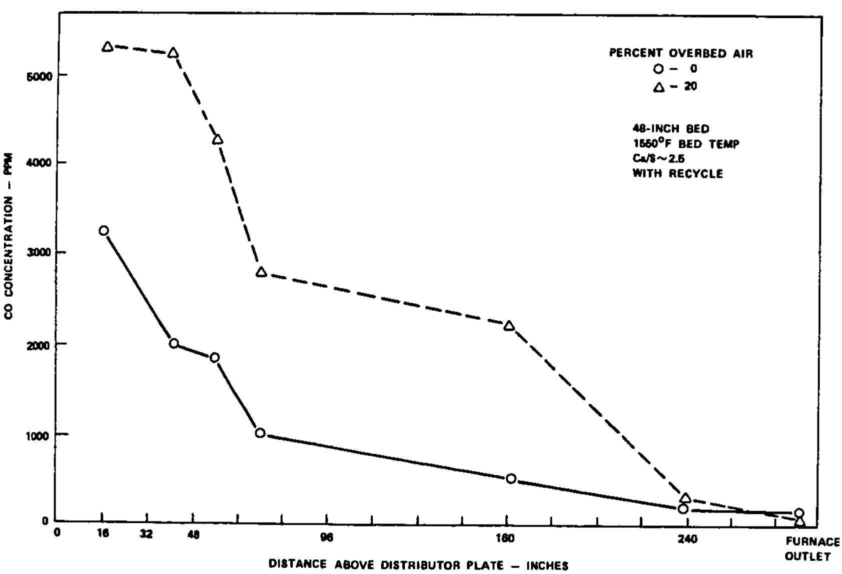


Figure 18 Average Carbon Monoxide Concentration as a Function of Distance Above the Distributor Plate

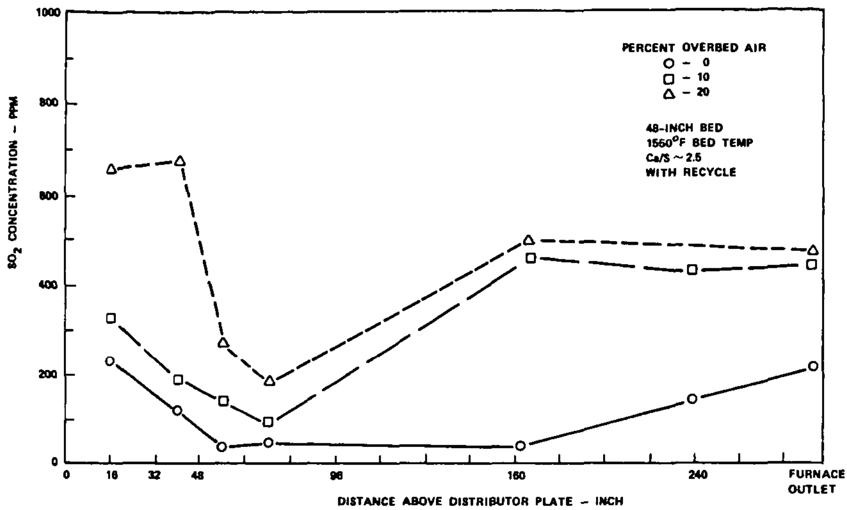


Figure 19 Average Sulfur Dioxide Concentration as a Function of Distance Above the Distributor Plate

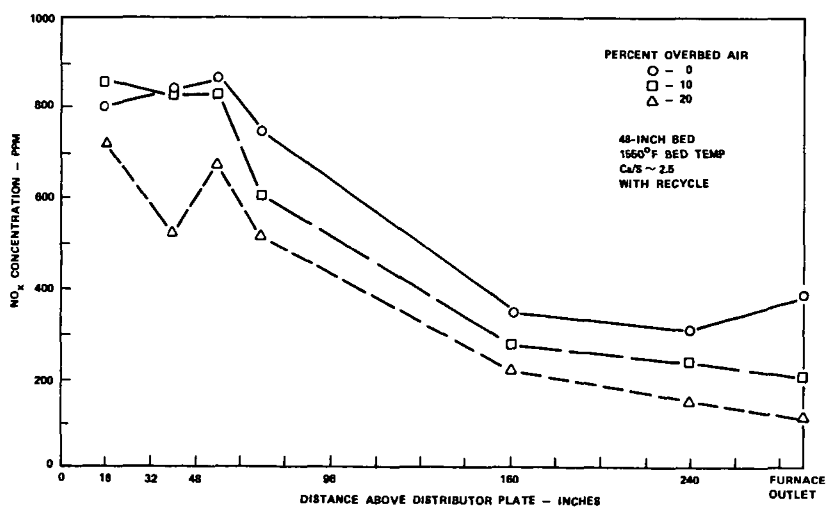


Figure 20 Average Nitrogen Oxide Concentration as a Function of Distance Above the Distributor Plate

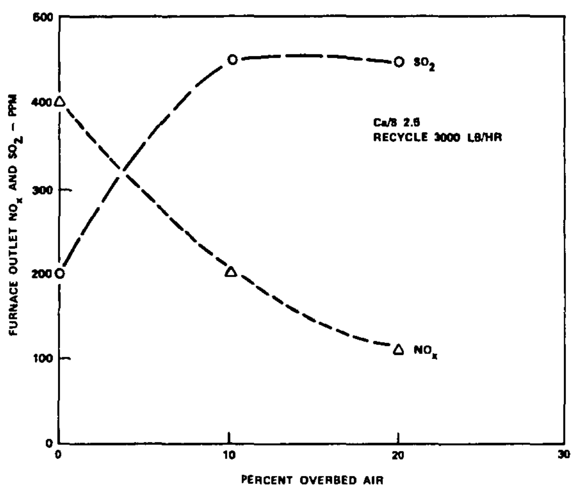


Figure 21 Measured Outlet Gas Concentrations at Various Percent Overbed Air Rates